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GRAPHENE-PEEK COMPOSITES AS HIGH TEMPERATURE ADHESIVES

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ABSTRACT

Polyetheretherketone is a widely used engineering polymer that is especially suitable for high-temperature applications. Graphene is a two-dimensional form of carbon nanomaterial that has been studied extensively for its mechanical, electrical and thermal properties and its use as a filler in polymer matrices. Compounding graphene into polymers has the potential to improve various properties, even at very low concentrations. In this work, we have examined the incorporation of graphene nanoplatelets (GnP) into PEEK. We have fabricated composites using melt-mixing techniques, as well as by graphene functionalization and in-situ polymerization of the PEEK. In this way, we can compare the performance of the composites by two different processing methods. The GnP-PEEK composites were characterized by DSC, TGA, and SEM. Lap-shear joints using the GnP-PEEK as the adhesive were made and mechanically tested. Results show that the weight fraction of GnP has a major effect on the strength of the joint. In this work, we aim to produce a material that functions as a reusable high-temperature, thermoplastic adhesive, which can be activated by conventional heating methods, or by microwave heating. The GnPs act as microwave absorbers and heat the surrounding PEEK matrix to the point of melting, in contrast to the neat PEEK, which does not melt upon exposure to the microwaves under the same parameters. The microwave absorption properties and adhesive properties will be presented.

TABLE OF CONTENTS

Abstract	i
Table of Contents	ii
List of Figures	iii
List of Tables	iii
1. Introduction.....	1
2. Composite Preparation.....	2
2.1 In-Situ Polymerization of PEEK.....	2
2.1.1 Functionalization of Graphene.....	2
2.1.2 PEEK Polymerization with Functionalized and Non-Functionalized Graphene	3
3. Composite Characterization.....	3
3.1 Microstructure Analysis.....	3
3.2 TGA/DSC	4
3.3 Preliminary Microwave Response Characterization.....	5
3.4 Lap Shear Testing	6
4. Conclusions.....	9
5. Acknowledgements.....	9
6. References.....	10

LIST OF FIGURES

Figure 1: Schematic representation of the concept	1
Figure 2: a) Electron microscopy image of 1 wt% GnP dispersed in PEEK. b) Higher magnification of GnP on the surface. The layered structure of the carbon sheets is clearly seen.	3
Figure 3: a) Electron microscopy image of 1 wt% GnP in PEEK, where the PEEK was formed by in-situ polymerization and b) 1 wt% of functionalized few-layer graphene in PEEK, where the PEEK was formed by in-situ polymerization. The PEEK polymerization is believed to start off the functional groups on the graphene, resulting in good bonding between the PEEK and graphene	4
Figure 4: a) Thermogravimetric analysis of polymerized PEEK with 1 wt% functionalized graphene and PEEK with 1 wt% GnP. b) Differential Scanning Calorimetry of polymerized PEEK with 1 wt% functionalized graphene and PEEK with 1 wt% GnP.....	5
Figure 5: 1wt% GnP-PEEK and Pure PEEK powder (white) exposed to microwaves	5
Figure 6: High-weight fraction PEEK/GnP composites (2, 5, 10, 35 wt% GnP) after exposure to microwaves. The 2, 5 and 10 wt% samples show bulk melting (center of specimens), while the 35 wt% shows melting/charring in the top left-hand corner	6
Figure 7: Lap shear specimen in Instron	6
Figure 8: Plot of the lap shear strength of the PEEK-GnP adhesive lap shear joints. The 2.0 wt% GnP adhesive showed the highest strength.....	7
Figure 9: Lap shear specimens of pure PEEK (left) and PEEK-1wt% GnP (right) after failure	8
Figure 10: SEM images of the cohesive failure region with clearly visible graphene nanoplatelets.....	8

LIST OF TABLES

Table 1: Results of Lap Shear Testing	7
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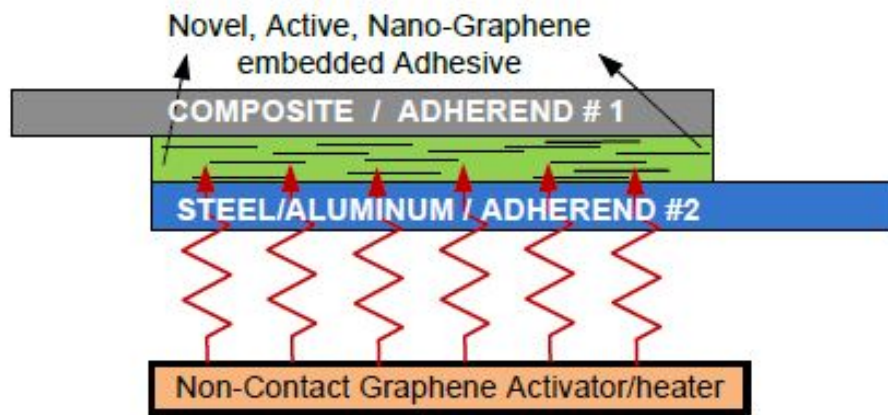


Figure 1. Schematic representation of the concept.

1. INTRODUCTION

Joining of composites can be a challenging issue. If adhesives are used, the joints are permanent and cannot be undone. If they need to be undone, inserts are often used and these inserts increase cost and weight. Additionally, fibers can be cut in the process leading to a part with weakened mechanical properties. Even with these drawbacks, most components that need to be joined are threaded together, allowing for removal of the parts at a later time. However, threaded connections are costly to design and manufacture, and are often the location of fatigue failures due to their inherent stress concentrations. From an environmental and cost standpoint, there is a large waste associated with the removal of material to form the threads, even more so in sector threads, where up to half of the machined thread is then cut away. Additionally, threaded joints often require grease to seal out environmental contamination and ensure that they can later be disassembled. This effort is aimed at replacing seldom-used threaded connections with a reusable thermoplastic adhesive.

The use of a thermoplastic makes the joining reversible, allowing any connection to be treated almost like a threaded joint, only one that uses heat instead of torque for activation. Recently, using thermoplastics as reusable adhesives has been researched by DoE for application in automobiles [1]. However, that work is focused on thermoplastics for room temperature applications, with no work being conducted on high temperature thermoplastics such as PEEK and Polyimide. The use of localized microwave radiation to heat the thermoplastic will eliminate the need for large furnaces which consume large amounts of time and energy, and ultimately heat other parts of the system that do not need to be heated. Our laboratory has begun investigating activation of high temperature thermoplastics using microwave radiation.

Figure 1 shows the basic concept. Two adherends are brought together with a graphene-doped thermoplastic between them. The assembly is then subjected to microwaves which excite the graphene nanoplatelets in the adhesive generating heat and causing the adhesive to melt. When the microwave source is removed, the adhesive solidifies joining the two materials. Since the

adhesive is a thermoplastic, subsequent applications of microwaves can be used to re-melt the adhesive and disassemble the assembly. For adherends that block microwaves, a wave guide would be needed to direct them to the bondline.

While various carbon species can absorb microwaves [2], nanospecies such as carbon nanotubes and graphene have been investigated most recently [3-5] because of their highly effective absorption at low weight loadings and ability to improve mechanical properties as well. Microwaves, when incident on an absorptive material, create heating by the interaction of the electromagnetic fields with the molecular and electronic structures of the molecules in the material exposed to the microwaves. The amount, and rate, of heating can be a function of microwave power, frequency, absorption, etc. We aim to study all these factors as we investigate microwaves as a heating source for high-temperature, reusable thermoplastic adhesives.

2. COMPOSITE PREPARATION

Melt-mixed GnP-PEEK composites, in-situ polymerized GnP-PEEK and graphene-PEEK composites have all been made. Dry powders of PEEK (Solvay Ketaspire KT-820FP, $T_m = 343$ °C, $T_g = 143$ °C) and 1 wt% graphene nanoplatelets (XG Sciences, Grade M) were mixed using a high speed mixer (Flacktek). GnPs are thicker (6-8 nm) than single or few-layer graphene (less than 1 nm). This uniformly mixed material was then melt compounded using a Haake torque rheometer. This is an intensive mixer with two counter rotating rotors and a temperature controlled barrel [6]. In addition to melt-mixing method, we have prepared composites using in-situ polymerization of the PEEK in the presence of GnP and few-layer graphene (functionalized and non-functionalized), which is described in more detail below. By studying various graphene species and fabrication methods, we will be able to select which method shows the best performance.

2.1 In-Situ Polymerization of PEEK

2.1.1 Functionalization of Graphene

Safety warning: The functionalization reaction makes use of an in situ diazonium salt. Diazonium salts are explosive and appropriate safety measure must be used for this reaction.

N002-PDR graphene (Angstrom Materials) with specific surface area of 600 m²/g and, thus, approximately 46% surface exposed carbons atoms was used for functionalization. A round bottom flask was loaded with N002-PDR graphene (150 mg, 1eq surface) and 4-aminophenol (2.51g, 2 eq). The flask was purged with argon and anhydrous tetrahydrofuran (50 mL) was added to the flask followed by iso-phenylnitrile (3.1 mL, 2eq). The reaction was allowed to proceed at 50°C for 22 h. The functionalized graphene was collected by centrifugation and washed with hexanes and ethyl acetate.

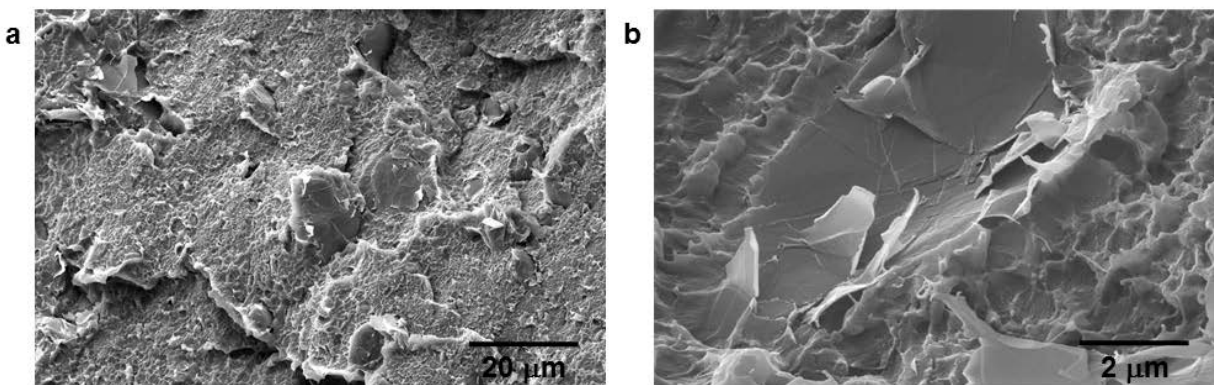


Figure 2. a) Electron microscopy image of 1 wt% GnP dispersed in PEEK. b) Higher magnification of GnP on the surface. The layered structure of the carbon sheets is clearly seen.

2.1.2 PEEK Polymerization with Functionalized and Non-Functionalized Graphene

A microwave synthesis vial (30mL) was loaded with hydroquinone (1.10g, 1eq), 4,4'-difluorobenzophenone (2.18g, 1eq), sodium carbonate (1.17g, 1.1eq), and functionalized graphene or graphene nanoplatelets (30mg, 1% wt product). 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (5 mL) was added to the vial. The vial was sealed and the reaction was carried out using a Monowave 400 microwave synthesizer (Anton Paar) at 300°C for 30 minutes using a ruby thermometer for temperature control. The resulting product was collected by centrifugation and washed by resuspension and centrifugation ten times alternating between water and acetone.

3. COMPOSITE CHARACTERIZATION

3.1 Microstructure Analysis

Electron microscopy (FEI Nanolab 600i) was performed on the samples in order to characterize the dispersion quality of the GnP and few-layer graphene in the composites. Figure 2 shows the 1 wt% GnP melt-mixed in the PEEK. Nanoplatelets are clearly seen in the fracture surface. Figure 3 shows the microstructure of PEEK-GnP (Fig. 3a) and PEEK-functionalized graphene (Fig. 3b), where the PEEK has been formed by in-situ polymerization. The PEEK is polymerized around the GnP, and it is believed to polymerize off of the functional groups in the case of the functionalized graphene. PEEK that is attached to the graphene through a functional group is expected to show improved thermal and mechanical properties, and perhaps, increased microwave absorption and heat transfer to the polymer.

3.2 TGA/DSC

Thermogravimetric analysis (TGA, TA Instruments TGAQ50) and Differential Scanning Calorimetry (DSC, TA Instruments DSC Q100) of the in-situ polymerized PEEK with 1 wt% functionalized graphene and 1 wt% GnP is shown in Figure 4. Both tests were conducted in a nitrogen atmosphere and heated at 5 °C/min and cooled at 20 °C/min. The high char content (residual weight % at 1000 °C) shows that the polymerization was successful in creating high molecular weight polymer chains [7]. The results also show that the functionalized graphene adds thermal stability (TGA curve shifted to the right) to the polymer. These preliminary tests indicate that the functionalized graphene could provide improved properties to the polymer compared to the larger GnP. The cooling curves for DSC are shown in Fig. 4b. The functionalized graphene material shows a solidification exotherm at 245 °C and the GnP composite shows one at 232 °C. The GnP shows a larger crystallization exotherm at 163 °C, and the graphene composite shows little-to-no exotherm at this temperature. This could be a result of the well-dispersed, high surface area graphene interacting with the polymer chains and creating a steric hindrance effect, where the PEEK chains do not have the mobility to move and form crystallites. This could result in competing effects during microwave exposure, where high absorptivity and heat transfer may lead to faster localized melting, but lower chain mobility delays bulk melting. These factors will be studied in more depth during future work.

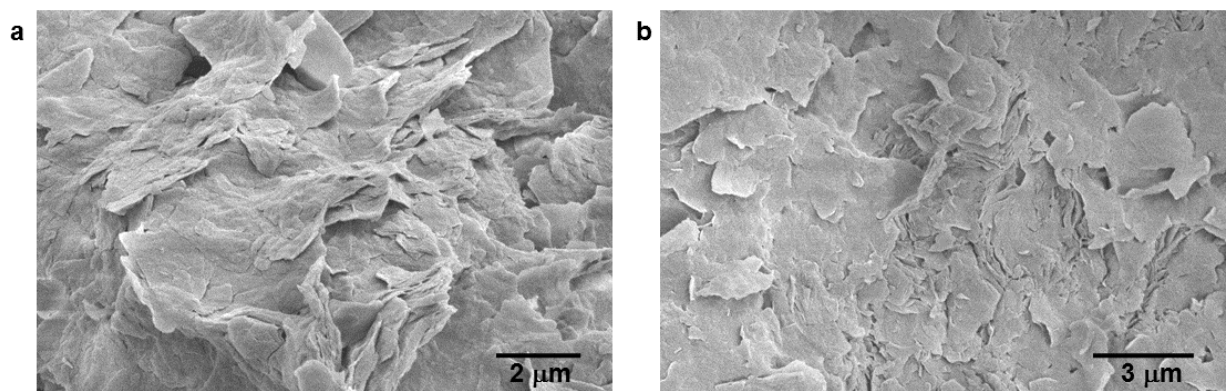


Figure 3. a) Electron microscopy image of 1 wt% GnP in PEEK, where the PEEK was formed by in-situ polymerization and b) 1 wt% of functionalized few-layer graphene in PEEK, where the PEEK was formed by in-situ polymerization. The PEEK polymerization is believed to start off the functional groups on the graphene, resulting in good bonding between the PEEK and graphene.

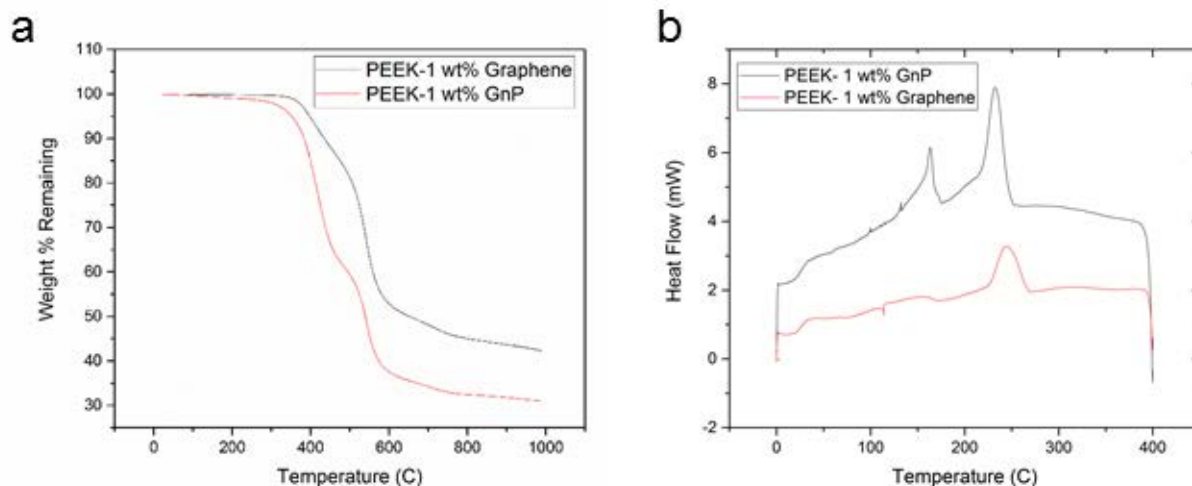


Figure 4. a) Thermogravimetric analysis of polymerized PEEK with 1 wt% functionalized graphene and PEEK with 1 wt% GnP. b) Differential Scanning Calorimetry of polymerized PEEK with 1 wt% functionalized graphene and PEEK with 1 wt% GnP.

3.3 Preliminary Microwave Response Characterization

Some preliminary tests have been conducted to observe the response of PEEK-GnP composites when exposed to microwaves.

Pure PEEK and 1 wt% GnP-PEEK was placed in a commercial microwave (1250W, 2.45 GHz) oven to see which would melt first. The 1 wt% GnP-PEEK absorbed the radiation and melted after tens of minutes. With its low absorption the pure PEEK did not melt before the test was stopped due to the turntable rotor melting (a low temperature plastic). Fig. 5 shows 1 wt% GnP-PEEK (black, melted) and pure PEEK (white powder, no melting).

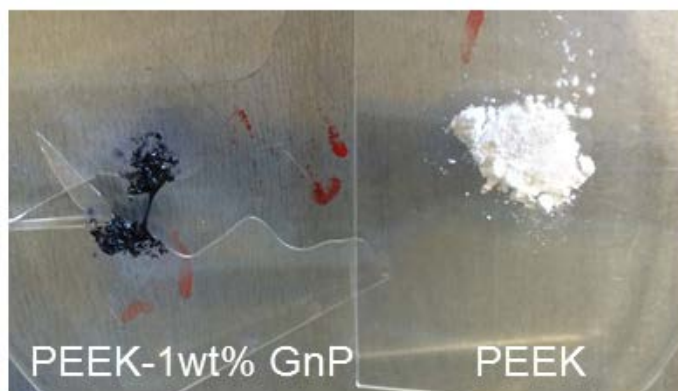


Figure 5. 1wt% GnP-PEEK and Pure PEEK powder (white) exposed to microwaves.

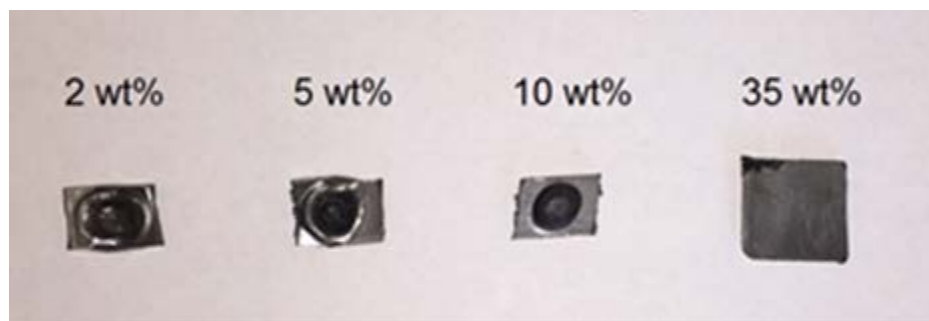


Figure 6. High-weight fraction PEEK/GnP composites (2, 5, 10, 35 wt% GnP) after exposure to microwaves. The 2, 5 and 10 wt% samples show bulk melting (center of specimens), while the 35 wt% shows melting/charring in the top left-hand corner.

In another test, we studied the microwave exposure of higher GnP content PEEK composites in a commercial microwave oven (780W, 2.45 GHz). Here, we see the 35 wt% sample begin to melt and ignite into flames within just a few seconds exposure. The 10, 5 and 2 wt% samples began to show bulk melting and bubbling by 2:56, 3:30 and 4:15 minutes, respectively. All samples (except the 35 wt%) had similar volumes. The samples, after melting, are shown in Figure 6.

It is clear that the amount of GnP in the composite has an effect on the microwave absorption behavior. Other factors that can play a role in absorption behavior are graphene type (platelet versus mono- or few-layer), degree of dispersion, functionalization, etc. Studying these factors in PEEK nanocomposites is a current topic of research in our laboratory.

3.4 Lap Shear Testing

A standard test for assessing the performance of an adhesive is a lap shear test. In this test two adherends are bonded together with a known overlap area and then pulled apart. We followed ASTM D1002 [8] for the testing and utilized aluminum adherends. The samples were made by taking two 203.2 mm (8 in) wide by 101.6 mm (4 in) long sheets of 2024 aluminum and overlapping them by 12.7 mm (0.5 in) in the 101.6 mm direction. In this overlap area a 0.127 mm (0.005 in) film of the adhesive was placed between the sheets. This thickness was picked as it as a customary bondline thickness we use. The assembly was then placed in platen press and heated to 357 C (675 F) at which time the pressure was increased to 2 MPa (290 psi) and then allowed to cool to room temperature. The plate was then sliced into a series of 25.4 mm (1 in) wide specimens.

Seven specimens each using pure PEEK, 1, 2, 5, 10 and 35 wt% GnP PEEK were fabricated this way. The pure PEEK samples were made using a 0.127 mm (0.005 in) purchased from McMaster-Carr. The 1 wt% film was made by taking small pieces of extruded material and placing them between mold released aluminum and running through the



Figure 7. Lap shear specimen in Instron.

same cycle mentioned in the previous paragraph. The 2, 5, 10, and 35 wt% films were made in a similar fashion only the starting materials were pieces of an injection molded dogbone.

Measurements of the individual specimen's dimensions and overlap area and thickness were taken. The specimens were then tested to failure using an Instron tensile test machine (Fig 7). Calculations were done according to ASTM D1002 to calculate failure strength. The results are given below in Table 1 and plotted in Figure 8.

Table 1 - Results of Lap Shear Testing

Material	Failure Strength	Std. Dev	Coeff. of Variation
PEEK	1.74 ksi	0.16 ksi	0.092
PEEK – 1 wt% GnP	1.72 ksi	0.07 ksi	0.041
PEEK– 2 wt% GnP	3.00 ksi	0.067 ksi	0.022
PEEK– 5 wt% GnP	2.71 ksi	0.031 ksi	0.011
PEEK–10 wt% GnP	2.15 ksi	0.127 ksi	0.059
PEEK–35 wt% GnP	1.09 ksi	0.068 ksi	0.062

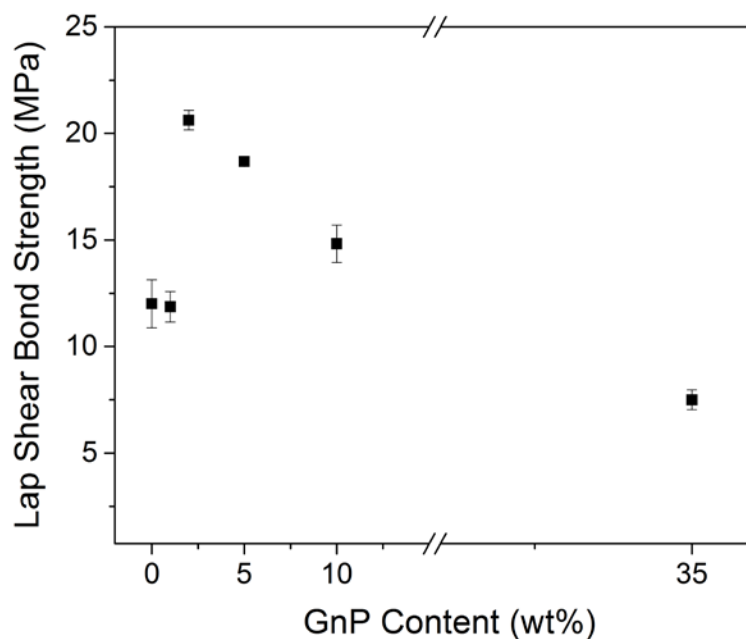


Figure 8. Plot of the lap shear strength of the PEEK-GnP adhesive lap shear joints. The 2.0 wt% GnP adhesive showed the highest strength.

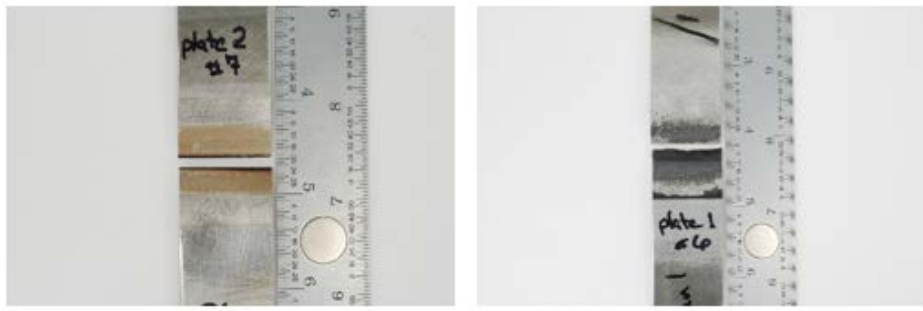


Figure 9. Lap shear specimens of pure PEEK (left) and PEEK-1wt% GnP (right) after failure.

Statistically, we see no difference between the 1 wt% GnP and pure PEEK. One possible reason for this is that the pure PEEK was purchased as a film whereas the 1 wt% was converted from extruded pieces to a film by repeatedly melting and compressing it on a heated platen press. This may have caused irregular dispersion of the graphene, porosity or uneven film thickness. SEM images of the dogbones showed the platelets were aligned in the X-Y direction and it is assumed that they stayed aligned during the filming and sample creation operations. The 2 wt% GnP composite shows the highest lap shear strength of all the samples (3.0 ksi), with a 72% improvement in strength over the pure PEEK joint. The 5 and 10 wt% GnP composites display a lower strength than the 2 wt% GnP, but are still higher than the pure PEEK. The highest weight fraction, 35 wt% GnP, shows a lap shear strength 38% lower than the pure PEEK. The 2 wt% loading appears to be close to an optimal loading for interalminar strength. As with any nano additive there is always a competition between adding material to increase properties vs. creating more inclusions for cracks to propagate from. As the wt% increases the particles will tend to agglomerate causing less uniform dispersion and thus increasing possible failure sites more than strength.

After the test the failure mechanism of the samples was looked at. In all cases the failure was cohesive with failed adhesive being evenly split between the two adherends, Figure 9 shows a

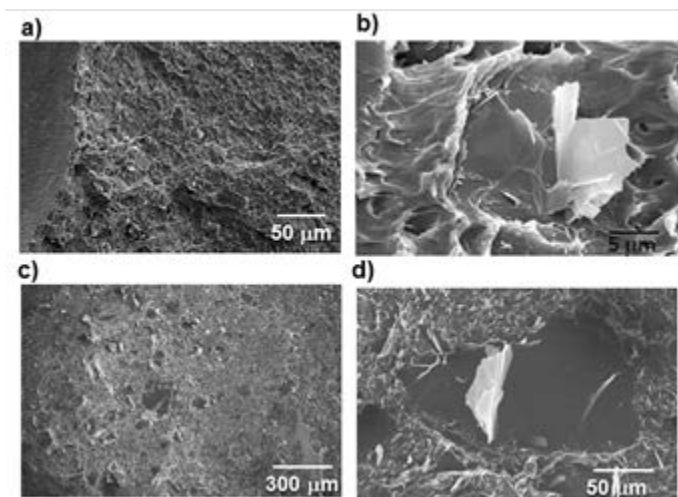


Figure 10. SEM images of the cohesive failure region with clearly visible graphene nanoplatelets.

PEEK (left) and 1 wt% GnP-PEEK sample after failure. Figure 10 shows SEM images of the cohesive failure region with clearly visible graphene nanoplatelets. In figure 10, SEM of the fracture surfaces for the 1 and 35 wt% samples are shown. While GnPs can be seen on both surfaces, the 35 wt% had large GnPs (hundreds of microns in size) on the surface. The platelets that are parallel to the lap shear direction contribute very little to the strength of the joint. Since weak van der Waal forces bond the graphene sheets together, large GnPs are easily sheared in the direction of the lap shear, which is evident in fracture surface images of Figure 10c and 10d.

4. CONCLUSIONS

In this study, we have examined various graphene species in PEEK as potential materials for a high-temperature adhesive. Preliminary microwave testing has shown that the graphene or graphene nanoplatelet composites can absorb microwaves to a level that will melt the PEEK, a property that could be useful in using microwaves as a localized heating source in a reusable thermoplastic adhesive application. Lap shear testing showed that the 2 wt% GNP had the highest lap shear strength, with a 72% increase in strength over the pure PEEK. The PEEK 35 wt% GNP showed the lowest strength of all the materials. Analysis of the fracture surface of the 35 wt% GNP material showed large areas of sheared nanoplatelets, up to hundreds of microns in size. These acted as points of weakness in the lap shear samples, leading to low joint strength. In addition, we show that in-situ polymerization is a viable option for fabricating PEEK-graphene composites. Further testing of these materials is needed to demonstrate the potential as a high-temperature adhesive material.

5. ACKNOWLEDGEMENTS

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